ON ENANTIOTROPY AND MONOTROPY. II.

By Noboru NAGASAKO.

Received August 18, 1928. Published September 28, 1928.

The behaviours of dimorphism at constant pressu e may be classified at least into three categories. The first is the case in which the transition occurs in the reversible manners or enantiotropy. The second is the case in which the transition is limited in one direction or monotropy. For the third we are able to consider a case in which the transition can not occur. In the preceeding paper[1] the typical thermodynamic relations for enantiotropy and monotropy were discussed in general and it was tried to supplement the studies in this field. In the present paper these relations will be discussed for the individual cases, especially in the case of monotropy.

The Thermodynamic Eormulae Concerning the Affinity of Transition. As for the unit mass of the substance in one component, we have the following relations concerning the $\chi-$ and $\zeta-$ functions of Gibbs,

$$\left(\frac{\partial \chi}{\partial T}\right)_p = c_p,$$

$$\zeta = \chi - Ts = \chi + T\left(\frac{\partial \zeta}{\partial T}\right)_p.$$

$$\left(\frac{\partial \zeta}{\partial T}\right)_p = -s \quad \text{and} \quad \left(\frac{\partial \zeta}{\partial p}\right)_T = v,$$

where s, v, c_p, are the entropy, the volume and the heat capacity at constant pressure respec ively concerning unit mass, p and T being pressure and absolute temperature. As the diffe ence of these quantities are always necessary, the difference of these functions as the result of a virtual transition at p and T, between the two modifications, $A \rightarrow B$ will be denoted by the corresponding large letters as follows, $Z=\zeta_B-\zeta_A$, $X=\chi_B-\chi_A$, $S=s_B-s_A$, $V=v_B-v_A$ and $C_p=c_{pB}-c_{pA}$, where X is the calorimetric heat of transition expressed after the manners of Berthelot and Thomsen and Z is often called the affinity of transition respectively concerning the transition $B \rightarrow A$.

It is evident that we have the following relations among these quantities,

(1) This journal, **3** (1928), 91.

$$\left(\frac{\partial X}{\partial T}\right)_p = C_p \qquad \text{(Kirchhoff's law)}$$

or $$X = X_0 + \int_0^T C_p dT \qquad \text{.....(1)}$$

and $$Z = X + T\left(\frac{\partial Z}{\partial T}\right)_p \qquad \text{(Gibbs and Helmholtz's law)}$$

or $$d\left(\frac{Z}{T}\right)_p = -\frac{X}{T^2} \ .$$

By the integration of the above equation at constant pressure, we have

$$\frac{Z}{T} = \frac{Z_{T_1}}{T_1} - \int_{T_1}^T \frac{X}{T^2} dT \ . \qquad \text{.....(2)}$$

If we let the transition temperature be $T_0\ (\neq 0)$, we have

$$Z = -T\int_{T_0}^T \frac{X}{T^2}\, dT \ . \qquad \text{..... (2a)}$$

If we assume after Nernst that

$$\lim_{T=0}\left(-\frac{\partial Z}{\partial T}\right)_p = \lim_{T=0} S = 0$$

or $$S = \int_0^T \frac{C_p}{T} dT \ ,$$

we have the following relations at constant pressure,

$$Z = Z_0 - \int_0^T S\, dT \qquad \left(\because \left(\frac{\partial Z}{\partial T}\right)_p = -S\right)$$

$$= Z_0 - \int_0^T dT \int_0^T \frac{C_p}{T} dT$$

$$= Z_0 - T\int_0^T \frac{dT}{T^2}\int_0^T C_p\, dT$$

$$= X_0 - T\int_0^T \frac{X - X_0}{T^2}\, dT \ . \qquad \text{.....(3)}$$

And we have $$\left(\frac{\partial Z}{\partial p}\right)_T = V \ .$$

By the integration at constant temperature, we have

$$Z = Z_{p_1} + \int_{p_1}^p V\, dp \ . \qquad \text{..... (4)}$$

The formulae (2) and (2a) show that we can estimate the affinity of transition within the range of temperature for which the specific heats of the

two modifications are known, the affinity and the heat of transition being observed at any temperature within it. On the other hand, the formula (3) shows that we are able to estimate the affinity of transition from absolute zero to any temperature if we know the specific heats for the corresponding range of temperature and the heat of transition at any temperature within it.

Evaluation of the Affinity of Transition. From the thermodynamic standpoint, the most thoroughly studied examples can be found in the dimorphism of sulphur[1] and tin.[2] In the former case, the affinity of transition was estimated on the basis of the Nernst's theorem or by the formula (3). In the latter case, it was evaluated by the formula (2a) or on the basis of the second law of thermodynamics, from the transition temperature down to absolute zero. As the result of which the Nernst's theorem was verified. The e are the typical cases of enantiotropy and the Z-curves (or affinity curves) are as in the Fig. 4 in the preceeding paper. In these cases the transition point is fairly clear and the affinity of transition may also be estimated directly by the measurement of solubility[3] or e.m.f.,[4] although the range of temperature is narrowly limited. Therefore, it is able to estimate the affinity of transition within a wide range of temperature on the mere basis of the second law of thermodynamics.

In the case of diamond and graphite, however, so far as the experiments are concerned, it is almost impossible to measure the affinity of transition directly. This system was first studied by Roozeboom[5] from the standpoint of phase theory and was ascribed to the category of pseudomonotropy, although its theoretical ground is not very accurate. It seems interesting to treat it on the basis of the Nernst's theorem, for by the sole means of which we are able to evaluate the affinity of transition quantitatively. Roth[6] observed the heat of transition as follows,

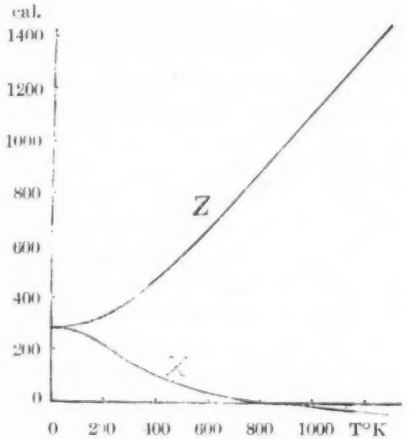
$$\text{Diamond} = \text{Graphite} + 156 \text{ cal./gr. atom.} \quad (\text{at } 290°\text{K.})$$

As for the specific heats of diamond and graphite, the Nernst's[7] data have been taken for the lower temperatures and the Magnus'[8] data for the higher temperatures from 300°K. to 1100°K. The values of the heat of transition have been calculated by means of the formula (1) from 0°K to 1100°K. Next, the values of the affinity of transition have been calculated by the formula (3). In the above calculations, the Debye's T^3 law has been applied for the

(1) W. Nernst, "Grundlagen des neuen Wärmesatzes" (1918), p. 87.
(2) J. N. Brönsted, *Z. physik. Chem.*, **88** (1914), 479. cf. F. Lange, ibid, **110** (1924) 343.
(3) J. N. Brönsted, ibid., **56** (1906), 645.
(4) E. Cohen, ibid., **30** (1899), 614.
(5) H. W. B. Roozeboom, "Die heterogenen Gleichgewichte" (1901), p. 179.
(6) W. A. Roth and H. Wallasch, *Z. Elektrochem.*, **21** (1915), 1.
(7) W. Nernst, *Ann. Physik*, **36** (1911), 396.
(8) A. Magnus and A. Hodler, ibid., **80** (1926), 808; A. Magnus, ibid., **70** (1923), 303.

calculation of the specific heats at the lowest temperatures, and the method of graphical integration has been used for the higher temperature. The results obtained are shown in the following table and in Fig. 1. In which X $\chi_{\text{diamond}}-\chi_{\text{graphite}}$ and $Z=\zeta_{\text{diamond}}-\zeta_{\text{graphite}}$. Therefore Z may be understood as the affinity of transition and X the heat of transition from diamond to graphite.

T°K.	X cal./gr. atom.	Z cal./gr. atom.
0	277	277
100	264	283
200	212	318
300	150	386
400	100	471
500	62	568
600	35	672
700	15	780
800	2	890
900	− 4	1007
1000	−16	1116
1100	−24	1230



Diamond and Graphite.
Fig. 1

These values will also be reproduced within the limits of a few percent if we apply the Debye's functions for the specific heats,

$$c_{p\ \text{diamond}}=D\left(\frac{1900}{T}\right)+1.9\times10^{-6}\,T^{\frac{3}{2}}\ ;$$

$$c_{p\ \text{graphite}}=\frac{1}{3}\left[2D\left(\frac{2280}{T}\right)+D\left(\frac{760}{T}\right)\right]+4.0\times10^{-6}\,T^{\frac{3}{2}}$$

where

$$D\left(\frac{\theta}{T}\right)=3Nk\left[\frac{12}{x^3}\int_0^x\frac{\xi^3d\xi}{e^\xi-1}-\frac{3x}{e^x-1}\right],$$

$$x=\frac{\theta}{T}=\frac{h\nu_{\max.}}{kT}\quad\text{and}\quad\xi=\frac{h\nu}{kT}\ .$$

The nature of the Z-curve in Fig. 1 shows that graphite is more stable than diamond in the range from 0°K. to 1100°K. And it is a well known fact that diamond is unstable at the higher temperatures above it. Out of these considerations, we are able to confirm that the dimorphism of diamond and graphite is truly monotropic, instead of being pseudomonotropic.

(1) P. Debye, *Ann. Physik*, 39 (1912), 789.
(2) Strictly speaking, it is necessary to add the condition, "under the atmospheric pressure," however, it will be omitted when clear.

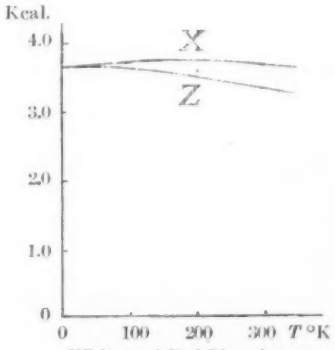
Furthermore, the *X*-curve in Fig. 1 shows that the heat of transition changes its sign at ca. 850°K. Above this temperature diamond seems to transform into graphite with the absorption of heat. It had been considered by some authors as one of the characteristic properties of monotropy that the unstable modification changes into the stable with the evolution of heat.(1) However, it may be mentioned here that even if there exist always stable and unstable modifications, the transition will not always occur with the evolution of heat, as is clear by the behaviours of *Z*- and *X*-curves in Fig. 1.

An analogical case will be found in the dimorphism of white and red phosphorus. As red phosphorus is nonvolatile and practically insoluble in many solvents below the ordinary temperature, it is also difficult to estimate the affinity of transition between them directly. Similar estimation on the basis of the Nernst's theorem have been carried out. As for the heat of transition, the Giran's(2) data have been taken,

Red phosphorus = White phosphorus + 3.70 Kcal./gr. atom (290°K.)

With regard to the specific heats, the data of Wigand(3) and Ewald(4) have been taken. The data of the specific heats are not very accurate in this case. However, the heat of transition is so large that the accuracy of the specific heats has no much influence upon the evaluation of the affinity of transition and the heat of transition. The results are shown in the following table and in Fig. 2, in which *Z* and *X* are the affinity and the heat of transition from white to red phosphorus respectively.(5)

T °K.	*X* Kcal./gr. atom	*Z* Kcal./gr.atom.
0	3.67	3.67
50	3.69	3.66
100	3.75	3.61
150	3.77	3.54
200	3.76	3.47
250	3.73	3.39
300	3.69	3.33



White and Red Phosphorus.
Fig. 2.

(1) H. W. B. Roozeboom, loc. cit.; cf. the quotation of O. Lehmann in the preceeding paper.
(2) Giran, *Ann. chim. phys.*, **30** (1903), 203.
(3) A. Wigand, *Ann. Physik*, **22** (1907), 64.
(4) R. Ewald, ibid., **44** (1914), 1213.
(5) As white phosphorus has a transition point at ca.–78°C., the white phosphorus above given is the form with the melting point at 44°C. cf. Bridgman, *J. Am. Chem. Soc.*, **36** (1914), 1244.

The affinity curve in Fig. 2 shows that red phosphorus is more stable than white phosphorus from absolute zero to the melting point of the white phosphorus. It is, therefore, truly monotropic, although it was supposed to be pseudomonotropic by Findlay.(1)

In certain cases of dimorphism, however, one modification exists in a very narrow range of temperature. So that the above given method to determine the relation ef mutual stability on the rigorous bases of the second law and the Nernst's theorem will fail, for the specific heats will not completely be measured. If the melting points and the latent heats of fusion of the both forms are known, however, we are able to derive an approximation formula for the estimation of the affinity of transition. After Nernst we may put, for the first approximation, that

$$X = X_0 + \beta T^2 \quad \text{and} \quad Z = X_0 - \beta T^2.$$

If we apply these formulae to the relations between the liquid phase and the modification A, we have

$$X_A = \chi_l - \chi_A = X_{A0} + \beta_A T^2, \qquad \cdots\cdots(5)$$

and

$$Z_A = \zeta_l - \zeta_A = X_{A0} - \beta_A T^2, \qquad \cdots\cdots(6)$$

where χ_l and ζ_l are the specific values of χ- and ζ-functions of Gibbs concerning the liquid phase respectively.

At the melting point T_A, we have $Z_A = 0$. Therefore, from (6), we have

$$\beta_A = \frac{X_{A0}}{T_A^2}.$$

Putting it in (5), we have

$$X_{A0} = \frac{1}{2}\lambda_A \quad \text{and} \quad \beta_A = \frac{1}{2}\frac{\lambda_A}{T_A^2},$$

where λ_A is the heat of fusion at the melting point T_A. Accordingly we have

$$Z_A = \frac{1}{2}\lambda_A - \frac{1}{2}\frac{\lambda_A}{T_A^2}T^2.$$

Similarly

$$Z_B = \frac{1}{2}\lambda_B - \frac{1}{2}\frac{\lambda_B}{T_B^2}T^2.$$

where $Z_B = \zeta_l - \zeta_B$, λ_B being the latent heat of fusion at the melting point T_B of the modification B.

Henceforth we have,

$$Z = \zeta_B - \zeta_A = Z_A - Z_B = X_0 - \beta T^2$$
$$= \frac{1}{2}(\lambda_A - \lambda_B) - \frac{1}{2}\left(\frac{\lambda_A}{T_A^2} - \frac{\lambda_B}{T_B^2}\right)T^2 \qquad \cdots\cdots(7)$$

(1) A. Findlay, "The Phase Rule" (1920), p. 48.

or $$X_0=\frac{1}{2}(\lambda_A-\lambda_B) \quad \text{and} \quad \beta=\frac{1}{2}\left(\frac{\lambda_A}{T_A^2}-\frac{\lambda_B}{T_B^2}\right).$$

Putting $Z=0$, we have the transition temperature T_0 between the two modifications A and B,

$$T_0=\left(\frac{\lambda_A-\lambda_A}{\frac{\lambda_A}{T_A^2}-\frac{\lambda_B}{T_B^2}}\right)^{\frac{1}{2}} \qquad \text{.....(8)}$$

With regard to the dimorphism of sulphur,[1]

$T_A=388°\text{K.}$, $\lambda_A=15.7$ cal./gr. (rhombic sulphur)
and $T_B=392°\text{K.}$, $\lambda_B=12.5$ cal./gr. (monoclinic sulphur)

Putting these values in the formulae (7) and (8), we have

$$Z=1.60-1.16\times10^{-5}T^2 \text{ cal./gr.,}$$
and $T_0=372°\text{K.}$ (obs. 368°K.)[2]

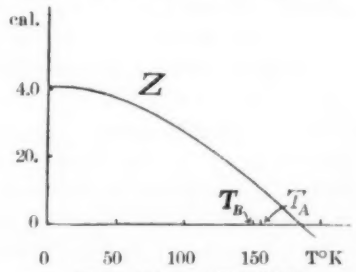
As for ethyl ether, we have following data,

$T_A=157°\text{K.}$, $\lambda_A=27.0$ cal./gr.,[3]
and $T_B=150°\text{K.}$, $\lambda_B=18.9$ cal./gr.[4]

Accordingly we have,

$$Z=4.05-2.53\times10^{-4}T^2 \text{ cal./gr.}$$
and $T_0=177°\text{K.}$ (above the melting points of the two modifications).

The values obtained by the above formula are shown in Fig. 3, which shows that the modification with the melting point at 150°K. is more stable than the modification with the melting point at 150°K., in the range from 0°K. to 177°K. We may therefore consider that this dimorphism of ethyl ether is monotropic.



Dimorphism of Ethyl Ether
Fig. 3

Although it is difficult to expect much accuracy from it, we are able to find that similar monotropic relations also hold for the dimorphisms in iodine monochloride,[5] benzophenone, bromonitrobenzene, phthalide, acetamide, monochloracetic acid, nitro-*p*-toluide and erythrite.[6] The values of X_0 and β are shown in the following table together with the data necessary for their evaluations.

(1) G. Tammann, "Kristallisieren und Schmelzen" (1903), p. 273.
(2) The results are in good coincidence with the estimation of Nernst, who obtained β by the data of specific heats.
(3) Beckmann and Waentig, *Z. anorg. allgem. Chem.*, **67** (1910), 17.
(4) S. Mitsukuri, this journal, **1** (1926), 30.
(5) Stortenbeker, *Z. physik. Chem.*, **10** (1892), 187.
(6) A. H. R. Müller, ibid., **86** (1913), 237.

Substance	T_A °K	λ_A cal./gr.	T_B K°	λ_B cal./gr.	X_0 cal./gr.	$\beta \times 10^5$
Iodine monochloride	300	16.4	287	14.0	1.20	0.60
Benzophenone	321	23.4	298	17.9	2.75	1.25
Bromonitrobenzene	332	29.3	308	21.0	4.15	2.75
Phthalide	346	39.4	333	20.0	9.70	7.40
Acetamide	355	66.1	344	57.0	4.55	2.05
Monochloracetic acid	334	40.7	329	35.2	2.75	1.85
Nitro-*p*-tolnide	366	30.0	365	26.7	1.65	1.15
Erythrite	390	43.7	377	38.0	2.85	1.00

In short, if the two modifications have a sharp transition point, it may be easy to ascribe it to enantiotropy. However, even if we observe the transition only in one direction within a limited range of temperature, it is rather difficult to ascribe it to monotropy. For the phase changes between the two modifications are often disturbed by the effects of retardation, and in certain occasions, the enantiotropic dimorphism may manifest itself like monotropic. It may form one of the cases of pseudomonotropy. Accordingly, if we would to ascribe any dimorphism to monotropy, the affinity of transition should be estimated over a wide range of temperature. Although we know of many cases supposed to be monotropic, the affinities of transition connected to them have not fully been testified so far. In the above discussions, it has been tried to estimate the affinity of transition for such cases.

Effects of Pressure on the Affinity of Transition. In the preceeding paragraphs, the effects of pressure on the mutual stability of dimorphism have not been estimated. The affinity of transition under high pressure will be estimated by the formula (4), by which it is meant that we are able to estimate the affinity of transition at any pressure p if we know the affinity of transition at certain pressure p_1 and the specific volumes of the two modifications between p_1 and p. Therefore, it may be able to determine whether or not it is enantiotropic under high pressure, if we know the affinity of transition at one atmospheric pressure and the necessary data of the specific volumes. As for the case of diamond and graphite, we have

$$V = v_{\text{diamond}} - v_{\text{graphite}}$$
$$= 12(1/3.5 - 1/2.3) = -1.79 \text{ cm.}^3\text{/gr. atom. (1 atm.)}$$

For the first approximation, we may put

$$\int_1^p V dp = pV$$
$$= -1.79\, p \text{ atm. cm.}^3\text{/gr. atom.} = -0.0433\, p \text{ cal./gr. atom.}$$

As we have gained (page 212) that $Z_{\text{298°K.}} = 386$ cal./gr. atom., and $\int_1^{10000} Vdp$

$= -433$ cal./gr. atom., we may consider that there will be a transition point at 300°K, under the pressure of ca. 10^4 atms. and that the case of diamond and graphite is probably enantiotropic under the pressure of ca. 10^4 atms. Whereas in the case of white and red phosphorus, the affinity of transition is enormous and $V = +3.17$ cm³/gr. atom (1 atm.). Therefore it will remain monotropic even under the farly high pressure.

In conclusion, the author wishes to express his hearty thanks to Prof. J. Sameshima whose counsels have been constantly at his disposal.

Summary

1. The affinity of transition and the heat of transition from diamond to graphite and from white phosphorus to red phosphorus have been evaluated on the basis of the Nernst's theorem and it has been made clear that they are monotropic under the atmospheric pressure. The former case will probably be enatiotropic under high pressure, whereas the latter case will remain monotropic even under high pressure.

2. An approximation formula for the estimation of the affinity of transition has been derived and by means of which the dimorphisms in ethyl ether, iodine monochloride, benzophenone, phthalide, bromonitrobenzene, acetamide, monochloracetic acid, nitro-*p*-toluide and erythrite have been estimated to be monotropic.

Chemical Institute, Faculty of Science,
Tokyo Imperial University.

ETHYL 1:2:3:6-TETRACARBETHOXY-5-METHOXY-$\Delta^{2,5}$-CYCLOHEXADIEN-1-ACETATE, A DERIVATIVE OF TRIETHYL ACONITATE.

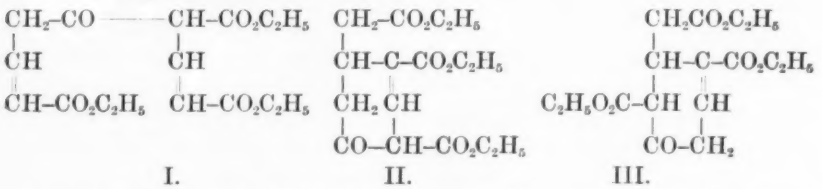
By Yoshiyuki URUSHIBARA.

Received July 24, 1928. Published September 28, 1928.

For a certain purpose the author tried the methylation of triethyl aconitate. A mixture of this ester and sodium ethylate in molecular proportion was heated on the water bath with an excess of methyl iodide in absolute alcoholic solution. As the reacting mixture was not brought to complete neutralisation in the course of one hour, it was heated at 115–120° under pressure. By this treatment the dark colour of the mixture faded to light brown. After concentrating the alcoholic solution, it was added to water

and extracted with ether. The ethereal extract gave a very viscous, fluorescent, slightly yellowish oil, which distilled at 225–230° under the pressure of about 1 mm.. It was purified by redistillation. 0.2220 Gr. of the substance gave 0.4632 gr. of CO_2 and 0.1340 gr. of H_2O ; 0.2929 gr. of the substance gave 0.6110 gr. of CO_2 and 0.1747 gr. of H_2O. (Found : C=56.92, 56.91 ; H= 6.75, 6.67%.) The numbers 491, 475, and 475 (mean 480) were obtained in the ebullioscopic determination of the molecular weight using acetone as the solvent. The analytical result corresponds to the formula $C_{23}H_{32}O_{11}$ which requires C=56.99, H=6.67%, and molecular weight=484. The obtained substance was not the methyl derivative of triethyl aconitate $C_{13}H_{20}O_6$ which requires C=57.31 ; and H=7.41%. If two molecules of triethyl aconitate $C_{12}H_{18}O_6$ split out one molecule of alcohol, and one hydrogen atom be substituted with a methyl group, that is, $2C_{12}H_{18}O_6 - C_2H_6O + CH_2$, the formula $C_{23}H_{32}O_{11}$ is obtained. Before entering the problem of the constitution of this substance, some statements on the condensation of diethyl glutaconate are indispensable.

E. E. Blaise[1] obtained a condensation product of diethyl glutaconate when he tried the methylation of this ester at a high temperature. He showed that this substance was formed by the action of sodium ethylate on the glutaconic ester, two molecules of the latter splitting one molecule of alcohol. He gave it formula I. To the same substance H. v. Pechmann, W. Bauer, and J. Obermiller[2] gave formula II, while R. Curtis and J. Kenner[3] accepted formula III.



I. II. III.

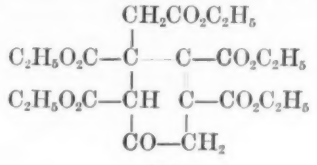
The last formula seems to be the most reasonable, and according to Curtis and Kenner this compound (in its enolic form) is called ethyl 2:6-dicarbethoxy-$\Delta^{2:5}$-cyclohexadien-5-ol-1-acetate. Blaise[4] tried the methylation of this compound and obtained a methyl derivative although not in a pure state.

In the present case, it is most probable that triethyl aconitate first gives the condensation product IV,[5] or, strictly speaking, its sodium derivative,

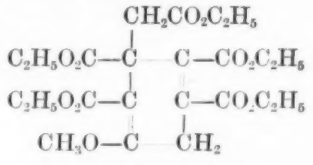
(1) *Bull. soc. chim.*, [3] **29** (1903), 1028.
(2) *Ber.*, **37** (1904), 2113.
(3) *J. Chem. Soc.*, **105** (1914), 282.
(4) Loc. cit.
(5) The mechanism of formation, cf. *Ber.*, **37** (1904), 2114.

and this is further methylated by the action of methyl iodide. Thus the compound with the formula $C_{23}H_{32}O_{11}$ is obtained. This substance does not dissolve in aqueous alkali, and gives no colouration on adding ferric chloride. It does not condense with phenylhydrazine by the same treatment as that which enabled Curtis and Kenner to obtain the phenylhydrazide of the compound represented by the formula III.[1]

This fact suggests that the methyl group in the compound $C_{23}H_{32}O_{11}$ is combined as a methoxy group, and that the intermediate product IV reacts in the enolic form, giving finally the methylated product V.



IV.



V.

Thus the constitution of the substance formed in the methylating reaction of triethyl aconitate at 115–120° is represented by the formula V, and may be called ethyl 1:2:3:6-tetracarbethoxy-5-methoxy-$\Delta^{2,5}$-cyclohexadien-1-acetate.

Chemical Institute, Faculty of Science,
Tokyo Imperial University.

SUPPLEMENTARY STUDIES ON THE NITRILE-ESTERS OF THE DICARBOXYGLUTACONIC ACID.[2]

By Yoshiyuki URUSHIBARA.

Received August 21, 1928. Published September 28, 1928.

Methyl Ethyl Dicyanoglutaconate.[3] The sodium derivative of this mixed ester is to be obtained (I) by the condensation of ethyl ethoxy-methylene-cyanoacetate with methyl sodio-cyanoacetate, and (II) by the condensation of methyl ethoxy-methylene-cyanoacetate with ethyl sodio-cyanoacetate, according to the following equations:

(1) Blaise states that he obtained phenylhydrazone of the substance formed by methylating the condensation product of diethyl glutaconate, but the present author does not believe the correctness of Blaise's view.

(2) For the completion of the studies published in this journal, **2** (1927), 278.

(3) Diethyl and dimethyl compounds: this journal, **2** (1927), 26, 236, 283.

(I) $C_2H_5OCO(CN)C{=}CH{-}OC_2H_5 + HCNa(CN)COOCH_3$
$= C_2H_5OCO(CN)C{=}CH{-}CNa(CN)COOCH_3 + C_2H_5OH,$

(II) $CH_3OCO(CN)C{=}CH{-}OC_2H_5 + HCNa(CN)COOC_2H_5$
$= CH_3OCO(CN)C{=}CH{-}CNa(CN)COOC_2H_5 + C_2H_5OH.$

As is evident from the above equations, the products of the two reactions are apparently different in the positions of the sodium atom and the double union, but it can be expected that they will prove to be identical as in the other cases.

Each of the condensations (I) and (II) was carried out (a) in ethyl alcohol and (b) in methyl alcohol. The experimental procedure common to these four kinds of reactions was as follows: Metallic sodium (1 mol) was dissolved in alcohol, the cyanoacetic ester (1 mol) was added, and then the ethoxy-methylene-compound (1 mol) was introduced. The sodium derivative of the dicyanoglutaconic ester separated out in yellow crystals. It was recrystallised from water, when it became nearly colourless, and then was transformed into the semihydrate by the action of dilute hydrochloric acid, which was examined.

(Ia) The product was wholly *diethyl* dicyanoglutaconate semihydrate $(C_{11}H_{12}O_4N_2)_2H_2O$ with the melting point 184°.

(Ib) The product was found to be *methyl ethyl* dicyanoglutaconate semihydrate with the melting point 197° (corr.). 0.2232 Gr. of the substance gave 23.6 c.c. of nitrogen at 18.5°, 761.0 mm. (Found: N=12.14. $(C_{10}H_{10}O_4N_2)_2H_2O$ requires N=12.12%.)

(IIa) The product was the same as that of (Ib). 0.1754 Gr. of the substance gave 18.45 c.c. of nitrogen at 18°, 762.4 mm. (Found: N=12.13%.) The specimens of (Ib) and (IIa) and their mixture melted at the same point 197°.

(IIb) The product was wholly *dimethyl* dicyanoglutaconate semihydrate $(C_9H_8O_4N_2)_2H_2O$ with the melting point 224°.

Thus it has been found that the cyanoacetic ester exchanges its alcohol group when it is converted into the sodium derivative by the action of sodium alcoholate. The exchange of the alcohol group can not take place in the products of the above condensations, for, when dimethyl sodio-dicyanoglutaconate was dissolved in ethyl alcohol, and the solution was boiled for one hour, none of the methyl groups was replaced by an ethyl group.

Mixed Esters of Dicarboxyglutaconic Acid. The condensation of dimethyl malonate with diethyl ethoxy-methylene-malonate was carried out (a) in ethyl alcohol, and (b) in methyl alcohol. The formed sodium compounds were recrystallised from ethyl alcohol. The free esters were obtained by the action of dilute hydrochloric acid in the aqueous solutions. In analysis, the product of (a) gave approximately the numbers calculated for *methyl triethyl*

ester. (Found: C=53.67; H=6.51. $C_{14}H_{20}O_8$ requires C=53.14; H=6.38%.) The product of (b) gave nearly the numbers for *dimethyl diethyl* ester. (Found: C=51.16; H=5.91. $C_{13}H_{18}O_8$ requires C=51.64; H=6.01%.)

The malonic ester also exchanges one of its alcohol groups when it is converted into the sodium derivative by the action of sodium alcoholate. Thus, after dimethyl malonate was acted by sodium ethylate, it reacted as if it were methyl ethyl malonate.

The Constitutions of the Sodium Derivatives of the Nitrile-esters of Dicarboxyglutaconic Acid. Those having symmetrical arrangement of cyano- and carbethoxy-groups afford no problem concerning their constitutions, and they are:

(I) $(C_2H_5OCO)_2C=CH-CNa(COOC_2H_5)_2$;
(II) $C_2H_5OCO(CN)C=CH-CNa(CN)COOC_2H_5$;
(III) $(CN)_2C=CH-CNa(CN)_2$.

The free ester, tetraethyl dicarboxyglutaconate, obtained by acidifying the aqueous solution of the sodium compound (I), gives blue colour on adding ferric chloride to its alcoholic solution, showing that it is, at least partly, in the enolic form.[1] Tetracyanopropylene $(CN)_2C=CH-CH(CN)_2$ obtainable in solutions from the sodium derivative (III) was found to give no colouration with ferric chloride. Since the free nitrile-ester corresponding to the sodium compound (II) is not obtainable,[2] another compound is to be examined instead of it, in order to know whether it would give colouration with ferric chloride or not, if it should exist. Fortunately, diethyl α, γ-dicyano-β-methyl-glutaconate $C_2H_5OCO(CN)C=C(CH_3)-CH(CN)COOC_2H_5$ is obtainable from its sodium derivative.[3] This substance was found to give no colouration with ferric chloride. Thus the compounds in which the carbon atom retaining the sodium atom possesses two carbethoxy-groups are characterised with the colouration. The ferric chloride test carried out directly on the sodium compunds (I), (II), and (III) in their alcoholic solutions led to the same conclusion.

Now, the constitutions of the sodium derivatives of the other nitrile-esters of dicarboxyglutaconic acid can be determined by the reaction with ferric chloride. By the previous investigation it was found that the condensation of diethyl ethoxy-methylene-malonate with sodio-malonitrile, and the condensation of ethoxy-methylene-malonitrile with diethyl sodio-malonate give the same sodium compound, from which the same diethyl dicarbamyl-proplylene-dicarboxylate is obtained. Then it was shown that the sodium

(1) H. Stobbe u. F. Wildensee, *J. prakt. Chem.*, **115** (1927), 163.
(2) This journal, **2** (1927), 26.
(3) This journal, **3** (1928), 102.

compound formed in the two reactions must have one of the two following formulae.

(IV) $(CN)_2C=CH-CNa(COOC_2H_5)_2$,

(V) $(CN)_2CNa-CH=C(COOC_2H_5)_2$;

but it was not decided which is the constitution of the substance. This sodium compound gives an oily deposit on acidifying its aqueous solution, which dissolves again in the mother liquor when it is left there for a while and is transformed into the crystals of diethyl dicarbamyl-propylene-dicarboxylate.

The oily substance deposited from the aqueous solution of the sodium compound was quickly extracted with ether and the ethereal solution was washed with water, dehydrated with calcium chloride, and evaporated in vacuo. The oily residue was dissolved in alcohol. This alcoholic solution gave bluish violet colour on adding ferric chloride, showing that the oily substance is in the enolic form. The sodium compound itself gave violet colour on adding ferric chloride to its alcoholic solution.

The oily substance from both the sodium derivative obtained by the condensation of diethyl ethoxy-methylene-malonate with sodio-malonitrile, and that obtained by the condensation of ethoxy-methylene-malonitrile with diethyl sodio-malonate, gave the same colouration with ferric chloride.

It is evident that the oily substance is the free nitrile-ester corresponding to the sodium compound. If it gives a colouration with ferric chloride, its constitution must be represented by formula (VI), or, in the enolic form, by formula (VII), and its sodium derivative by formula (IV).

(VI) $(CN)_2C=CH-CH(COOC_2H_5)_2$, diethyl γ,γ-dicyano-propylene-α,α-dicarboxylate;

(VII) $(CN)_2C=CH-\underset{\underset{COOC_2H_5}{|}}{C}=C(OH)OC_2H_5$.

The alcoholic solution of this enolic cyano-ester gave a colourless crystalline deposit on standing for a while. After this transformation it gave no colouration with ferric chloride. It was also experienced that the colour given by a fresh alcoholic solution on adding ferric chloride faded gradually. The crystals were collected, washed with alcohol, and dried in a desiccator. This crystalline substance melts at 212°. 0.1149 Gr. of the substance gave 0.2185 gr. of CO_2 and 0.0580 gr. of H_2O; 0.0608 gr. of the substance gave 5.85 c.c. of nitrogen at 18°, 758.5 mm. (Found: C=51.88; H=5.65; N=11.03. $C_{11}H_{12}O_4N_2\cdot H_2O$ requires C=51.95; H=5.55; N=11.03%.) The analytical result corresponds to the monohydrate of diethyl dicyano-propylene-dicarboxylate, and one of the cyano-groups is hydrated into a carbamyl-group.

Of course, it has the configuration of diethyl γ-cyano-γ-carbamyl-propylene-α, α-dicarboxylate, $H_2NCO(CN)C=CH-CH(CO_2C_2H_5)_2$, and, therefore, the dihydrate[1] is diethyl γ, γ-dicarbamyl-propylene-α, α-dicarboxylate, $(H_2NCO)_2C=CH-CH(CO_2C_2H_5)_2$. While the enolic nitrile-ester is gradually transformed into the ketonic form, it is at the same time changed into the dicarbamyl compound in the aqueous solution, and into the monocyano-monocarbamyl compound in the alcoholic solution.

Triethyl cyano-propylene-tricarboxylate (cyano-carboxyglutaconate) gives violet colour on adding ferric chloride to its alcoholic solution. Hence formula (VIII) must be assigned to this cyano-ester, and formula (IX) to its sodium derivative.

(VIII) $C_2H_5OCO(CN)C=CH-CH(COOC_2H_5)_2$, triethyl γ-cyano-propylene-α, α, γ-tricarboxylate;

(IX) $C_2H_5OCO(CN)C=CH-CNa(COOC_2H_5)_2$, triethyl α-sodio-γ-cyano-propylene-α, α, γ-tricarboxylate.

The examples already described suggest that the sodium atom is generally retained by the carbon atom with the most carbethoxy-groups. For this reason the constitution of the ethyl sodio-tricyano-propylene-carboxylate may be represented by formula (X).

(X) $(CN)_2C=CH-CNa(CN)COOC_2H_5$, ethyl α-sodio-α, γ, γ-tricyano-propylene-α-carboxylate.

The compounds obtained by the action of a dilute acid on the sodium compounds, the free nitrile-esters or the various hydrates,[2] may be considered to have the same configurations as the corresponding sodium derivatives. There has been nearly nothing to suggest the configuration of methyl ethyl sodio-dicyanoglutaconate.

The Mechanism of the Condensation of an Ethoxy-methylene Compound $C_2H_5OCH=CXY$ with a Methylene Compound $CH_2X'Y'$ in the Presence of Sodium Alcoholate. In the previous paper on the nitrile-esters of the dicarboxyglutaconic acid, the mechanism of the condensation of an ethoxy-methylene compound with a sodio-methylene compound (or methylene compound in the presence of sodium alcoholate) was explained on the assumption that Thorpe's theory of the normal form can be applied to the derivatives of dicarboxyglutaconic acid. But this theory was found to be based on uncertain evidences and it is natural to consider that the α- and γ-positions in the glutaconic acids are not identical.[3] Now that explanation

(1) This journal, **2** (1927), 281.

(2) Strictly speaking, they should not be called hydrates, for the water combined in those compounds can not be removed, showing that it is not the water of crystallisation.

(3) This journal, **3** (1928), 205.

must be corrected according to this fact. In that and also in this paper it was shown that the condensation of $C_2H_5OCH=CXY$ with $CHNaX'Y'$, and the condensation of $C_2H_5OCH=CX'Y'$ with $CHNaXY$, where X, X', Y, and Y' represent any of the negative groups such as CN and $COOC_2H_5$, give one and the same product, while two with the following formulae can be expected:

(XI) $XYC=CH-CNaX'Y'$,
(XII) $X'Y'C=CH-CNaXY$.

Even a slight difference in the groups attached to each end of the propylene chain caused the seeming migration of the double union, only one compound free from the isomeride being produced in sufficient yield.

On the other hand, Hope[1] found clearly a difference between the two following derivatives of glutaconic acid:

(XIII) $C_2H_5OCO(CN)C=C(CH_3)-CH(CH_3)COOC_2H_5$,
(XIV) $C_2H_5OCO(CN)CH-C(CH_3)=C(CH_3)COOC_2H_5$.

He observed that the former is only very slowly transformed into the latter by the action of ammonia. By the action of sodium ethylate the former is also transformed into the sodium derivative of the latter, but only partly.

It may be supposed it is not impossible that the methyl group in the β-position of the compounds investigated by Hope prevented the double union from moving, and enabled the two isomerides to exist, and that, as there is no methyl group in the condensation product of an ethoxy-methylene compound with a sodio-methylene compound, the migration of the double union can easily take place.

But it has been found that this view is contradictory to the fact, for the condensation of methyl ethoxy-ethylidene-cyanoacetate with ethyl sodio-cyanoacetate and the condensation of ethyl ethoxy-ethylidene-cyanoacetate with methyl sodio-cyanoacetate gave the same product, while two corresponding to the following formulae are expected:

(XV) $CH_3OCO(CN)C=C(CH_3)-CNa(CN)COOC_2H_5$,
(XVI) $C_2H_5OCO(CN)C=C(CH_3)-CNa(CN)COOCH_3$.

The details of the experiments will be given later in another paper.

Therefore, it is reasonable to suppose that the double union can not easily move after it has been once formed. Then how is the mechanism of the condensation in question explained? Suppose that an ethoxy-methylene compound and a methylene compound give, in the first place, an addition compound in the presence of sodium alcoholate, the elimination of alcohol and substitution of hydrogen with sodium taking

(1) *J. Chem. Soc.*, 121 (1922), 2216.

	Condensations	Sodium compounds obtained by the condensations	Compounds obtained by the action of an acid on the sodium compounds
(1)	$4NaOMe + 2CH_2(CO_2Me)_2 + CHCl_3$	$(MeO_2C)_2C{:}CH{\cdot}CNa(CO_2Me)_2$	$(MeO_2C)_2C{:}CH{\cdot}CH(CO_2Me)_2$
(2)	$4NaOEt + 2CH_2(CO_2Et)_2 + CHCl_3$	$(EtO_2C)_2C{:}CH{\cdot}CNa(CO_2Et)_2$	$(EtO_2C)_2C{:}CH{\cdot}CH(CO_2Et)_2$
(3)	$4NaOEt + 2CH_2(CO_2Et)_2 + CCl_4$		
(4)	$4NaOEt + 2CH_2(CO_2Et)_2 + Cl_3CCO_2Et$		
(5)	$NaOEt + CH_2(CO_2Et)_2 + EtOCH{:}C(CO_2Et)_2$		
(6)	$NaOMe + CH_2(CO_2Me)_2 + EtOCH{:}C(CO_2Et)_2$	$C_{13}H_{17}O_8Na$	$C_{13}H_{18}O_8$
(7)	$NaOEt + CH_2(CO_2Me)_2 + EtOCH{:}C(CO_2Et)_2$	$C_{14}H_{19}O_8Na$	$C_{14}H_{20}O_8$
(8)	$NaOEt + CNCH_2CO_2Et + EtOCH{:}C(CO_2Et)_2$	$EtO_2C(CN)C{:}CH{\cdot}CNa(CO_2Et)_2$	$EtO_2C(CN)C{:}CH{\cdot}CH(CO_2Et)_2$
(9)	$NaOEt + CH_2(CO_2Et)_2 + EtOCH{:}C(CN)CO_2Et$		
(10)	$NaOEt + CH_2(CN)_2 + EtOCH{:}C(CO_2Et)_2$	$(CN)_2C{:}CH{\cdot}CNa(CO_2Et)_2$	$(CN)_2C{:}CH{\cdot}CH(CO_2Et)_2$ $H_2NCO(CN)C{:}CH{\cdot}CH(CO_2Et)_2$ $(H_2NCO)_2C{:}CH{\cdot}CH(CO_2Et)_2$
(11)	$NaOEt + CH_2(CO_2Et)_2 + EtOCH{:}C(CN)_2$		
(12)	$4NaOMe + 2CNCH_2CO_2Me + CHCl_3$	$MeO_2C(CN)C{:}CH{\cdot}CNa(CN)CO_2Me$	$(C_9H_8O_4N_2)_2H_2O$
(13)	$4NaOEt + 2CNCH_2CO_2Et + CHCl_3$	$EtO_2C(CN)C{:}CH{\cdot}CNa(CN)CO_2Et$	$(C_{11}H_{12}O_4N_2)_2H_2O$
(14)	$4NaOEt + 2CNCH_2CO_2Et + CCl_4$		
(15)	$4NaOEt + 2CNCH_2CO_2Et + Cl_3CCO_2Et$		
(16)	$NaOEt + CNCH_2CO_2Et + EtOCH{:}C(CN)CO_2Et$		
(17)	$NaOEt + CNCH_2CO_2Me + EtOCH{:}C(CN)CO_2Et$	"	"
(18)	$NaOMe + CNCH_2CO_2Me + EtOCH{:}C(CN)CO_2Et$	$C_{10}H_9O_4N_2Na$	$(C_{10}H_{10}O_4N_2)_2H_2O$
(19)	$NaOEt + CNCH_2CO_2Et + EtOCH{:}C(CN)CO_2Me$		
(20)	$NaOMe + CNCH_2CO_2Et + EtOCH{:}C(CN)CO_2Me$	$MeO_2C(CN)C{:}CH{\cdot}CNa(CN)CO_2Me$	$(C_9H_8O_4N_2)_2H_2O$
(21)	$NaOEt + CH_2(CN)_2 + EtOCH{:}C(CN)CO_2Et$	$(CN)_2C{:}CH{\cdot}CNa(CN)CO_2Et$	$(C_9H_7O_2N_3)_2H_2O$
(22)	$NaOEt + CNCH_2CO_2Et + EtOCH{:}C(CN)_2$		
(23)	$NaOEt + CH_2(CN)_2 + EtOCH{:}C(CN)_2$	$(CN)_2C{:}CH{\cdot}CNa(CN)_2$	$(CN)_2C{:}CH{\cdot}CH(CN)_2$
(24)	$4NaOEt + 2CH_2(CN)_2 + CHCl_3$		$(C_9H_8ON_4)_2H_2O$

place subsequently, then how two different condensations give the same prouct will be well understood.

$$\left.\begin{matrix} XYC{=}CHOC_2H_5+CH_2X'Y' \\ X'Y'C{=}CHOC_2H_5+CH_2XY \end{matrix}\right\} \xrightarrow{NaOC_2H_5} XYCH{-}\underset{\displaystyle OC_2H_5}{\underset{|}{CH}}{-}CHX'Y' \xrightarrow{NaOC_2H_5}$$

$XYC{=}CH{-}CNaX'Y'$ or $X'Y'C{=}CH{-}CNaXY$.

The hydrogen in the carbon with less cyano-groups is substituted with sodium, while the hydrogen in the carbon with more cyano-groups is splitted off forming ethyl alcohol with the ethoxy-group.

Summary. The table shows the outlines of synthetical studies made by the present author and others in regard to the nitrile-esters of dicarboxyglutaconic acid. The water of crystallisation which is present in some of the sodium compounds is omitted. The configurations of those written in molecular formulae are not yet known. As to the constitution of those written in the formula $(\ldots\ldots)_2H_2O$, see this journal, **2** (1927), 29. The details will be found in the following places:

(1) Guthzeit, Weiss and Schoefer, *J. prakt. Chem.*, **80** (1909), 439.
(2) Conrad, Guthzeit, *Ber.*, **15** (1882), 2842; *Ann.*, **222** (1884), 250.
(3) Zelinsky, Doroschewsky, *Ber.*, **27** (1894), 3374; Bischoff, *Ber.*, **28** (1895), 2829.
(4) Ruhemann, *Ber.*, **29** (1896), 1017.
(5) Claisen, Haase, *Ann.*, **297** (1897), 88.
(6), (7) Urushibara, this journal, **3** (1928), 220.
(8), (9) Errera, *Ber.*, **31** (1898), 1243; Urushibara, this journal, **2** (1927), 280; **3** (1928), 223.
(10), (11) Urushibara, this journal, **2** (1927), 281.
(12) Urushibara, this journal, **2** (1927), 240.
(13) Errera, *Ber.*, **31** (1898), 1241; Ruhemann, Browning, *J. Chem. Soc.*, **73** (1898), 282; Urushibara, this journal, **2** (1927), 28, 236.
(14) Dimroth, *Ber.*, **35** (1902), 2882.
(15) Urushibara, this journal, **2** (1927), 237.
(16) Urushibara, this journal, **2** (1927), 240, 283.
(17), (18), (19), (20) Urushibara, this journal, **3** (1928), 219.
(21), (22) Urushibara, this journal, **2** (1927), 284.
(23) Urushibara, this journal, **2** (1927), 285.
(24) Zörnig, *J. prakt. Chem.*, **74** (1906), 435.

The author expresses his hearty thanks to Prof. K. Matsubara for his kind inspection of this paper.

Chemical Institute, Faculty of Science,
Tokyo Imperial University.

ON THE BASIC NITROGEN COMPOUNDS FROM FUSHUN SHALE TAR. II.[1]

By Takashi EGUCHI.

Received August 25, 1928. Published September 28, 1928.

It is very clear, from the previous paper,[2] that the light fraction from Fushun shale tar, consists, for the greater part, of the basic compounds of the pyridine series, being rich in the α and γ alkyl derivatives. A complete chemical examination should be made of the bases in order to get more precise knowledge of the constituents, and to find more satisfactory data on the constants of the pyridine bases by isolating them in a state of purity, since the data which have been reported for these compounds are often regarded as contradictory in their discordancies, and many even of the simple derivatives are still left awaiting identification, notwithstanding, that a great deal of work in that field has been set forth in the literature.[3]

4-Methylpyridine. The presence of 4-methylpyridine in coal tar has already been recognized by K. E. Schulze,[4] A. Ladenburg,[5] O. Flaschner,[6] and many others but the fact seems to have been left alone by workers on the shale tar bases. The procedure followed in the preparation of this base has been, as in the case of other lower members of pyridine series, generally carried out by first refining the characteristic double salts of mercury or zinc-chloride, and then by regenerating and drying the free base. The mercuric chloride-method, however, includes much difficulty in the separation of the 3- and 4-methylpyridines in their fractions, for no marked features which might be utilised in such a practice, are recognized between them. Attempts were made to isolate 4-methylpyridine from the mixture of 2 : 6-dimethyl, 3-, and 4-methylpyridines by the aid of mercuric chloride but proved unsuccessful so far as the writer's experiments were concerned.

The base was accordingly treated successively with an insufficient amount of picric acid in alcohol, the crystallization being performed in a

(1) Contribution from the Scientific Research & Experimental Branch, Imperial Naval Fuel Depot, No. 2.

(2) This journal, **2** (1927), 176.

(3) V. Meyer & P. Jacobson, "Lehrbuch d. organ. Chem.", II, 3, p. 782-1047 ; N. V. Sidgwick, "The Organic Chemistry of Nitrogen", (1910); P. E. Spielmann, "The Constituents of Coal Tar", (1924) ; R H. McKee, "Shale Oil", (1925); C. Hollins, "The Synthesis of Nitrogen Ring Compounds", (1924); A. R. Warnes, "Coal Tar Distillation and Working up of Tar Products", (1923).

(4) *Ber.*, **20** (1887), 411.

(5) Ibid., **21** (1888), 287.

(6) *J. Chem. Soc.*, **95** (1909), 668.

thermostat with very great caution. Three kinds of picrate were formed; (1) a dark yellow rhombic thick plate, m.p. 160°–162°, (2) a light yellow thin plate, m.p. about 155°, (3) a dark yellow prism, m.p. about 125°, which appeared in the last stage. On recrystallizing the picrate (2) from boiling alcohol, flat needles, gathering in tufts, grew to several mm. in length showing a m.p. of 165°; 44 gr. of the picrate again recrystallized from 600 c.c. of boiling ethyl alcohol, 41 gr. of a very slender prism with a m.p. of 167° resulted, which remained constant after further recrystallization. The base regenerated from 40 gr. of the purified picrate was dried over fused potash. yield 10.9 gr.

The base resembles 2 : 4-dimethylpyridine in odour, and is completely miscible with water at room temperature. It distils completely at 145.45°–145.47° under 763.9 mm. The physical constants are; $d_4^{25}=0.9502$ (in vac.); $n_D^{25}=1.5029$; $n_C^{25}=1.4986$; $n_F^{25}=1.5143$; $n_{G'}^{25}=1.5240$.

0.1115 Gr. subst. gave 0.0756 gr. H_2O & 0.3165 gr. CO_2. 0.1753 Gr. subst. gave 22.5 c.c. N_2 at 18° & 761 mm. (Found: C=77.42; H=7.59; N=15.08. C_6H_7N requires C=77.36; H=7.58; H=15.05 %)

The base was identified as 4-methylpyridine from its oxidation product being proved to be isonicotinic acid; 1.7 gr. of the base was oxidised with 6 gr. of potassium permanganate; the filtrate from manganese oxide was treated with copper acetate after being neutralised with dilute sulphuric acid and 1.7 gr. of a blue microscopic crystalline powder deposited. Analysis shows: Found: C=38.09; H=4.53; Cu=16.69. $(C_5H_4N\,CO_2)_2Cu.4H_2O$ requires C=37.92; H=4.25; Cu=16.74 %.

The free acid from the salt, recrystallized from water, has a m.p. of 315° when rapidly heated, but all sublimes without melting when slowly heated in a capillary. It has no colour reaction with ferrous sulphate.

0.1055 Gr. free acid gave 0.0395 gr. H_2O & 0.2256 gr. CO_2. (Found: C=58.32; H=4.19. $C_5H_4N.COOH$ requires C=58.51; H=4.10 %).

Some salts of the base were examined: $C_6H_7N{\cdot}HCl{\cdot}AuCl_3$—slightly sol. in cold, but moderately in hot water, m.p., 218°; $C_6H_7N{\cdot}HCl{\cdot}2HgCl_2$—needles; m.p., 130°.

3-Methylpyridine. 3-Methylpyridine is a possible constituent of various kinds of tar bases and has many records of being isolated[1] from them and synthesised.[2]

In view of the observations made during the investigation, mercuric

(1) H. Weidel, *Ber.*, **12** (1879), 2008; J. Mohler, ibid., **21** (1888), 1009; O. Flaschner, *J. Chem. Soc.*, **95** (1909), 668; J. G. Heap, W. I. Jones & J. G. Speakman, *J. Am. Chem. Soc.*, **43** (1921), 1936.

(2) E. Zanoni, *Ber.*, **15** (1882), 528; L. Storch, ibid., **19** (1886), 2456; P. Schwarz, ibid., **24** (1891), 1676.

chloride is not recommendable for isolation of the base in a pure state, as is the case with γ-picoline, because the work does not always prove successful. The purification, therefore, was carried out as in the preceding experiment with picrate.

The melting-point of picrate (3) written in the former section was raised to 149° by repeated crystallizations in alcohol, which in total, amounted to 41.5 gr.

The base regenerated and dried over fused potash was 11.3 gr. It has somewhat a sweetish odour and completely distils at 144.17°–144.18° under 763.0 mm. pressure, and shows $d_4^{25}=0.9518$ (in vac.); $n_D^{25}=1.5038$; $n_C^{25}=1.4994$; $n_F^{25}=1.5155$; $n_{G'}^{25}=1.5256$.

It yields the following double salts with metallic chlorides:

$(C_6H_7N\cdot HCl)_2PtCl_4$,	m.p., 208°.
$C_6H_7N\cdot HCl\cdot AuCl_3$,	a pale yellow fibre, melts at 187°.
$C_6H_7N\cdot HCl\cdot HgCl_2$,	long needles melting at 145°–146°.
$C_6H_7N\cdot HCl\cdot 2HgCl_2$,	m.p., 146°.
$C_6H_7N\cdot HCl\cdot 3HgCl_2$,	produced when treated with excess of $HgCl_2$, white granular crystalls with a m.p., 170°.

The base was proved to be 3-methylpyridine by the analysis of the base and its oxidation products, as follows:

0.1025 Gr. base gave 0.0700 gr. H_2O & 0.2901 gr. CO_2. 0.1851 Gr. base gave 23.6 c.c. N_2 at 17° & 761 mm. (Found: C=77.19; H=7.65; N=15.04. C_6H_7N requires C=77.36; H=7.58; N=15.05%).

The base (1.4 gr.) was oxidised with the calculated amount of potassium permanganate (5 gr.); the free nicotinic acid crystallizes from hot water in a white mass, has no colour reaction with ferrous sulphate, partly, sublimes without decomposition and has a m.p. of 236°.

0.1050 Gr. subst. gave 0.2250 gr. CO_2, & 0.0397 gr. H_2O. (Found: C=58.44; H=4.23. Theory: C=58.51; H=4.10%).

The copper salt was a bright blue crystalline powder, and gave on analysis,

C=45.83; H=2.78; Cu=20.77. $(C_5H_4N\cdot CO_2)_2Cu$ requires C=46.81; H=2.62; Cu=20.66%.

2:3-Dimethylpyridine. F. C. Garrett and J. A. Smythe[1] have already proved the existence of this base in Scottish shale oil by isolating it with the aid of mercuric chloride in a certain grade of purity.

The method of procedure described in their report, however, is not appropriate in this case for getting it free from other isomers such as 2:5-dimethylpyridine, etc., owing to difficulty in obtaining it in a definite form

(1) *J. Chem. Soc.*, **81** (1902), 449; **83** (1903), 763.

with mercuric chloride. The picric acid method, in this respect, is superior to the mercuric chloride method in handling such bases.

The procedure for the isolation of this base from the fraction, b.p. 158°–160°, in which 2:4–lutidine and 2:6–collidine had been found, is briefly described below.

The fraction was dissolved into ten parts of hot alcohol. It yielded immediately a light yellow crystalline powder on adding picric acid dissolved in hot alcohol; and next, with some picric acid, gave partly the same crystals and partly flat needles. The former picrate has a m.p. of 188° after recrystallization from an excess of boiling alcohol. The free base regenerated from the picrate is a colourless liquid with a faint characteristic odour, soluble in 10 parts of water at 23°. It completely distils at 160.7° under 760 mm. The constants are: $d_4^{25}=0.9419$; $n_D^{25}=1.5057$; $n_C^{25}=1.5014$; $n_F^{25}=1.5172$; $n_{G'}^{25}=1.5272$.

It was identified as 2:3–dimethylpyridine by analysis and by converting into quinolinic acid by oxidation.

0.1794 Gr. of the base gave 20.4 c.c. N_2 at 25°.0 & 762 mm. (Found: N=13.05. C_7H_9N requires N=13.08%).

It yields a double salt with mercuric chloride, $C_7H_9N\cdot HCl\cdot 6HgCl_2$ m.p. 194°.

The acid obtained in a free state from its copper salt shows an orange-red colour with ferrous sulphate, and a m.p. of 247° when slowly heated in a capillary, but by rapid heating sinters at about 190° and then melts at 233°.

0.1385 Gr. subst. gave 0.0386 gr. H_2O & 0.2575 gr. CO_2. (Found: C=50.71; H=3.12. Theory: C=50.28; H=3.02%).

2:5–Dimethylpyridine.[1] During the course of the fractional crystallization, shown in the foregoing section, the writer obtained flat needles, to a fair amount, after a powdery picrate of 2:3–dimethylpyridine had been removed, and this, on decomposing with an alkali, gave quite a different odour from those of the dimethylpyridines described above, but rather resembling that of β–picoline, which in connection with the odours of the β–methylpyridines affords some idea, that it might be 2:5–dimethylpyridine.

Twenty three grams of the pure salt with a m.p. of 167° obtained by repeating the recrystallization from hot alcohol, yielded 5 gr. of the free base.

It is a colourless liquid with a sweetish odour, less pungent than β–picoline. It boils constantly at 156.82°–156.88° under 759.1 mm. and is soluble in 12 parts of water at 23°. The physical constants are: $d_4^{25}=0.9261$ (in vac.); $n_D^{25}=1.4982$; $n_C^{25}=1.4939$; $n_F^{25}=1.5095$; $n_{G'}^{25}=1.5194$.

(1) G. Lunge & J. Rosenberg, *Ber.*, **20** (1887), 134; F. C. Garrett, & J. A. Smythe, *J. Chem. Soc.*, **81** (1902), 453.

It yields the salts: $(C_7H_9N\cdot HCl)_2PtCl_4$ (214°); $C_7H_9N\cdot HCl\cdot 6HgCl_2\cdot H_2O$ (203°).

The base was noticed to be the same compound as the 2:5–dimethylpyridine, which were synthesised by G. Errera,[1] and for comfirmation it was analysed and then oxidized by the usual method to isonicotinic acid.

0.1071 Gr. subst. gave 0.0826 gr. H_2O & 0.3070 gr. CO_2. 0.1838 Gr. subst. gave 20.6 c.c. N_2 at 21° & 763 mm. (Found: C=78.18; H=8.64; N=13.07. C_7H_9N requires C=78.45; H=8.47; N=13.08%).

The free acid recovered from the copper salt of pale blue colour, is almost insoluble in cold water, slightly in hot, but more soluble in hot hydrochloric acid. When recrystallized from dilute hydrochloric acid it melts at 254°, while from boiling alcohol, it melts at 238° (with decomposition).

The free acid on analysis, responded as a pyridine-dicarboxylic acid with one mol of the water of crystallization.

0.1129 Gr. of the free acid lost 0.0105 gr. on drying. 0.1024 Gr. of the dried acid gave 0.0295 gr. H_2O & 0.1869 gr. CO_2. (Found: C=49.78; H=3.23; combined water=9.30. $C_7H_5O_4N\cdot(H_2O)$ requires C=50.27; H=3.02; combined water=9.74%).

3:5–Dimethylpyridine.[2] The presence of 3:5–dimethylpyridine in a coal tar base, has already been proved by F. B. Ahrens[3] and his co-workers.

The writer has also succeeded in isolating it, with the aid of picric acid, from the fraction b. p. 170°–172° of shale tar base in a pure state. The base which was isolated from the picrate has a faint odour somewhat resembling horse urine and β–picoline. The physical constants of the dried base are: b. p. 171.6° (760 mm.); $d_4^{25}=0.9385$; $n_D^{25}=1.5032$; $n_C^{25}=1.4988$; $n_F^{25}=1.5146$; $n_{G'}^{25}=1.5244$.

0.1033 Gr. subst. gave 0.0771 gr. H_2O & 0.2964 gr. CO_2. (Found: C=78.37; H=8.36. C_7H_9N requires C=78.45; H=8.47%).

The base yields by oxidation, nicotinic acid which melts at 327°. see errata V. 9, P. 321

0.1097 Gr. subst. gave 0.2016 gr. CO_2 & 0.0313 gr. H_2O. (Found: C=50.12; H=3.19. $C_7H_5O_4N$ requires C=50.28; H=3.02%).

3:4–Dimethylpyridine. In view of certain relations between the chemical structure of compounds and their physical constants being symphonious, the data exhibited by the series of pyridine homologues which the writer has isolated in a highly pure state, are likely to be of value in affording excellent examples, especially in offering a distinct regularity displayed by the boiling points; that is, if the hydrogen atom combined with the α–position of pyridine is replaced by a methyl group, the rise of the boiling-point is approxi-

(1) G. Errera, *Ber.*, **34** (1901), 3691.
(2) E. Dürkopf & H. Gottsch, *Ber.*, **23** (1890), 1113.
(3) Ibid., **37** (1904), 2064.

mately one-half as compared with that of the β or γ–methyl derivative. 3:4–Dimethylpyridine, which is the only one left awaiting identification among the theoretical dimethylpyridines, as the others have been already isolated in a pure state by the writer, was discovered by pursuing it in the fraction of b.p. 178°–180°, with the expectation that the boiling point would not be lower than that of 3:5–dimethylpyridine, though we find it lower than that in the literature.(1)

The fractions boiling at 177°–178° (25 gr.) and at 178°–179° (30 gr.) were treated with the calculated amount of picric acid in boiling methyl alcohol and slowly cooled, producing three kinds of crystals, which separated mechanically into

(1) upper crop of needles or prisms, m.p. 114°,

(2) middle crop of aggregates of small needles, m.p. 120°–140°, and

(3) bottom crop of prisms, m.p. about 163°.

The picrate which has a m.p. of about 163° was the main product in each case, and 19.4 gr. of the pure salt of m.p. 163° by recrystallizing twice from methyl alcohol were obtained.

The free base is a colourless liquid with a faint aromatic odour, soluble in 20 parts of water at 22°, and distilling completely at 178.82° under 759 mm., and yields the following salts:

$(C_7H_9N\cdot HCl)_2PtCl_4$,	orange-red prism, m.p. 276° (decomp.)
$C_7H_9N\cdot HCl\cdot 3HgCl_2\cdot 2H_2O$,	slender needles, easily soluble in hot, but only slightly in cold water, (Hg. found 60.66; theory 60.72; m.p. 130.5°–131°)
$C_7H_9N\cdot HCl\cdot AuCl_3$,	fern-like crystals, m.p. 187°.

It gave the constants: $d_4^{25}=0.9537$ (in vac.); $n_D^{25}=1.5099$; $n_C^{25}=1.5055$; $n_F^{25}=1.5209$; $n_{G'}^{25}=1.5305$.

The base was identified as 3:4–dimethylpyridine, by analysis of the base and also by the oxidation to cinchomeronic acid with a m.p. of 265°–266°.

0.1016 Gr. of the base gave 0.0766 gr. H_2O & 0.2920 gr. CO_2. 0.1512 Gr. of the base gave 17.6 c.c. N_2 at 24° & 758 mm. (Found: C=78.38; H=8.44; N=13.09; mol. wt.=108.6. C_8H_9N requires C=78.45; H=8.47; N=13.08%; mol. wt.=107.1).

0.1081 Gr. of the free acid gave 0.0306 gr. H_2O & 0.1997 gr. CO_2. (Found: C=50.38; H=3.17. $C_5H_3N\cdot(CO_2H)_2$ requires C=50.28; H=3.02%).

2:4–Methyl-ethylpyridine.(2) In the fraction of 178°–180°, the writer has found 2:4–methylethylpyridine presumably together with 2:6–parvoline from an amorphous picrate.

The fraction, which removed 3:4–dimethylpyridine etc. by means of

(1) *Ber.*, **29** (1896), 2996.

(2) H. Weidel & B. Pick, *Ber.*, **18** (1885), Ref. 117; M. Schultz, ibid., **20** (1887), 2720.

picric acid in alcohol, consisted mostly of a base forming an oily picrate. The oily picrate contaminated with crystalline picrates was separated mechanically from the latter after standing in an open vessel for six months in a dark and cool place.

The base recovered from the oily picrate was about a half of the original sample in the fraction of 178°–180°, and is a colourless liquid with a highly disagreeable odour incomparable to those of the methylpyridines, and soluble in water to a slight degree. The constants are: b.p.=179°–180°; $d_D^{25}=0.9130$; $n_D^{25}=1.4953$.

The main portion of the base was considered to be 2:4–methylethylpyridine on the whole, as it was oxidised to a lutidinic acid with a m.p. of 246°, though the results of combustion and mean molecular weight determination slightly exceeded the values for collidine.

Found: C=79.42; H=9.37; mol. wt.=126. C_7H_9N requires C=79.27; H=9.16%; mol. wt.=121.

Found: C=45.03; H=3.96. $C_7H_5O_4N\cdot H_2O$ requires C=45.39; H=3.81%.

2:3:6–Trimethylpyridine. If an idea which is based on the fact that the methyl group attached to the carbon atoms of the pyridine nucleus has some definite effects upon the boiling points of the methyl derivatives of pyridine, be extended to the higher members of the series, the boiling point of 2:3:6–trimethylpyridine would be considered to stand near with that of 2:4:6–trimethylpyridine which is the main constituent in the fraction b.p. 170°–172°. The attempt, therefore, was advanced to find it out in that fraction which, after the most of the 2:4:6–trimethylpyridine had been removed with mercuric chloride, was found to consist of a mixture of the bases when they were regenerated from the double salts. The bases which were recovered from the salts were colourless liquids with highly disagreeable odour which produced three kinds of crystalline picrates on treating them successively with an insufficient amount of picric acid in alcohol, viz.,

(1) light yellow needles of 2:4:6–trimethylpyridine picrate, m.p. 156°,
(2) a powdery picrate of 3:5–dimethylpyridine with a m.p. of 241°,
(3) a large hexahedron, orange in colour, easily crystallizable from alcohol, m.p., about 147°, with a yield of 48 gr.

The third picrate was purified twice from boiling methyl alcohol, yielding 41 gr. of the salt with a m.p. of 147°–148°.

The base regenerated from the salt by usual method and dried over fused potash, boils at 172.88°–172.90° under 761.2 mm., and is soluble in 32 parts of water at 26°.

The constants are: $d_4^{25}=0.9220$ (in vac.); $n_D^{25}=1.5018$; $n_C^{25}=1.4976$; $n_F^{25}=1.5133$; $n_{G'}^{25}=1.5232$.

It gave the following salts:

$C_8H_{11}N\,HCl{\cdot}AuCl_3$,	scales or needles, m.p. 139°,
$(C_8H_{11}N{\cdot}HCl)_2PtCl_4$,	blackens from about 220°,
$C_8H_{11}N{\cdot}HCl\,2HgCl_2{\cdot}H_2O$,	a slender prism, m.p. 104° (Hg. found, 56.3; theory, 55.8%),
$C_8H_{11}N\,HCl{\cdot}6HgCl_2$,	white granular crystals, m.p. 165° (Hg. found, 66.7; theory, 66.7%).

For identification it was analysed with the following results:

0.1118 Gr. of the base gave 0.0918 gr. H_2O & 0.3247 gr. CO_2. 0.1947 Gr. of the base gave 19.7 c.c. N_2 at 25° & 759 mm. (Found: C=79.21; H=9.19; N=11.58. $C_8H_{11}N$ requires C=79.27; H=9.16; N=11.50%).

The acid obtained from the base by oxidation with a potassium permanganate solution is extremely soluble in water, and shows a deep orange-red colouration with ferrous sulphate, which on neutralizing with a dilute sodium carbonate solution changes to a beautiful carmine-red. It melts at 245° with decomposition and agrees with 2:3:6-pyridinetricarboxylic acid written in the literature.(1)

(*To be continued on next page*)

(1) L. Weiss, *Ber.*, 19 (1886), 1305.